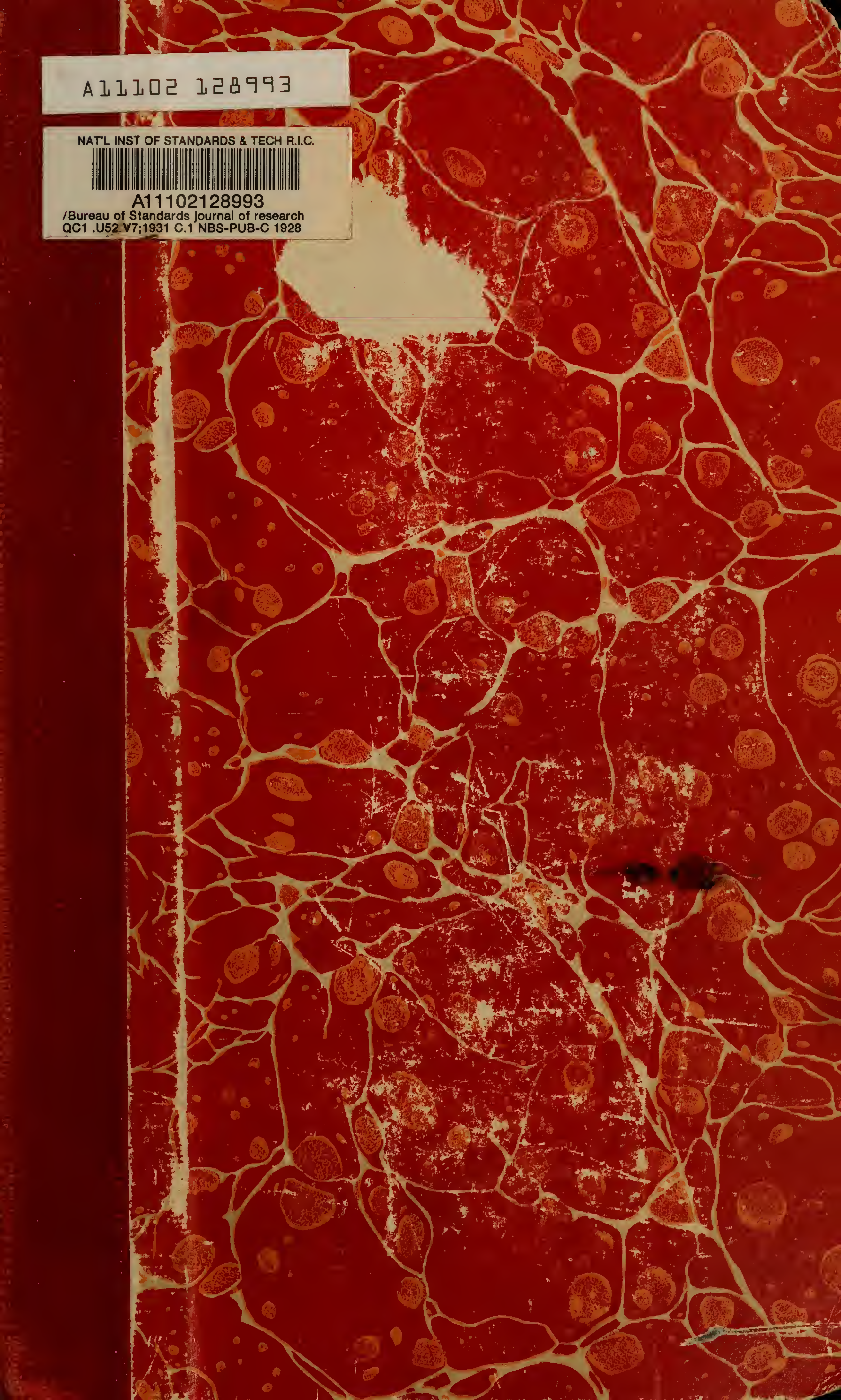

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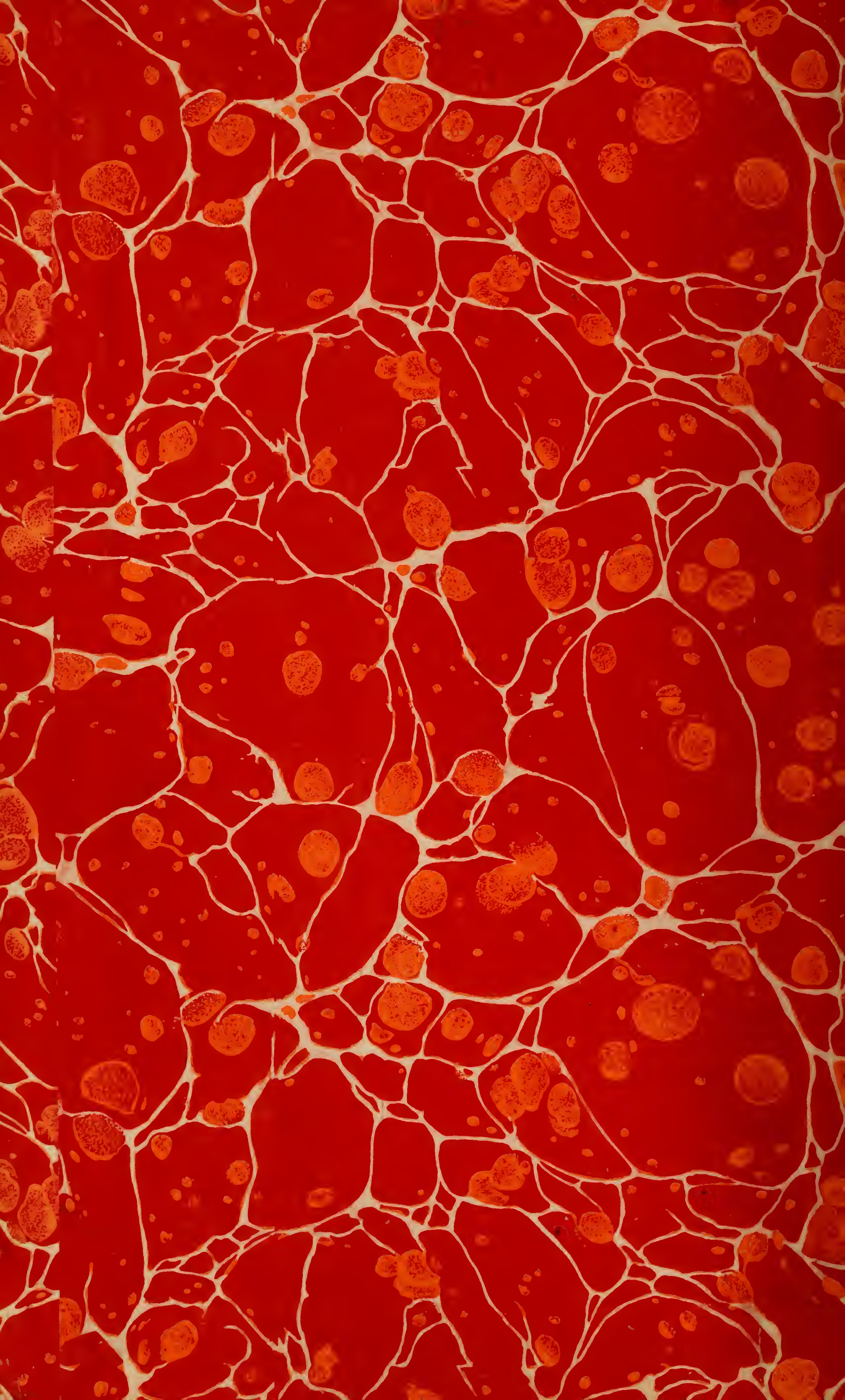

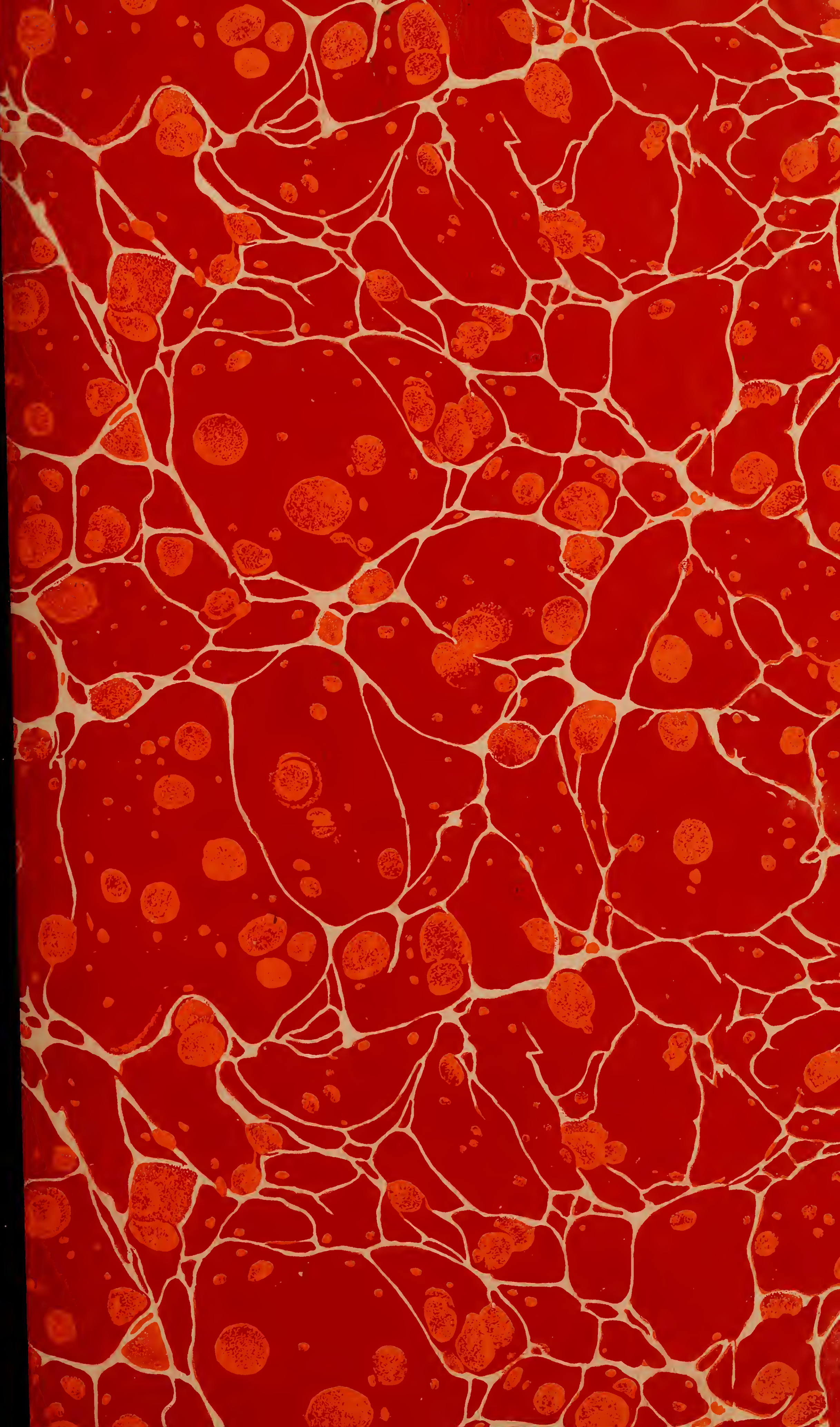

RP382

THE DETERMINATION OF THE COEFFICIENT OF CUBICAL EXPANSION OF SOLID BENZOIC ACID BY MEANS OF A GAS-FILLED DILATOMETER

By E. R. Smith

ABSTRACT

By measurement with a constant-volume gas-filled dilatometer the coefficient of expansion of benzoic acid between 15° and 30° C. was found to be 0.00052 per degree C.

For use in another investigation it was necessary to know the coefficient of cubical expansion of benzoic acid at room temperatures. Since no determinations of this quantity could be found in the literature, measurements were made from 15° to 30° C.

The method employed consisted in measuring the pressure at different temperatures of a definite amount of dry air inclosed in a flask with a relatively large quantity of prefused benzoic acid, keeping the total volume of the system constant.

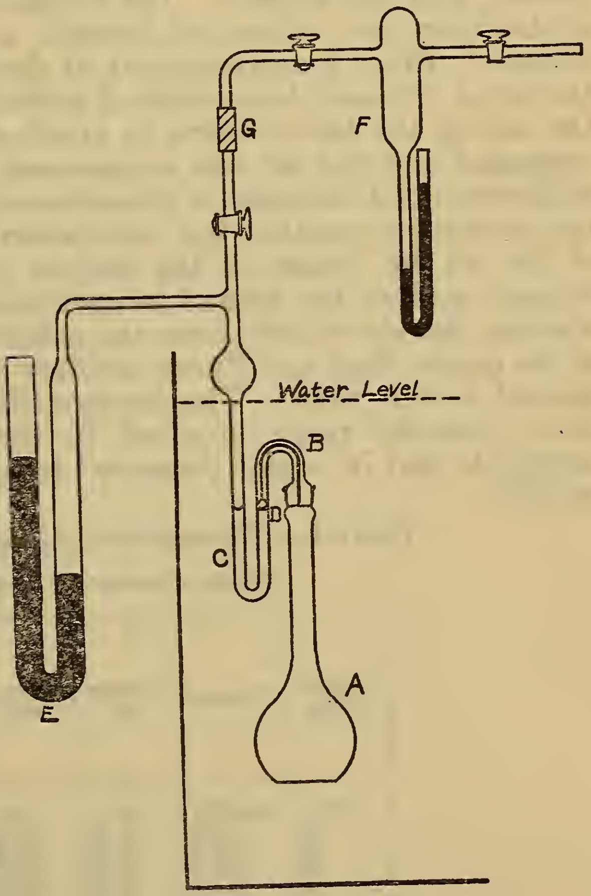

Figure 1.—*Apparatus for measuring coefficients of expansion*

The apparatus is shown in Figure 1. Benzoic acid (Bureau of Standards Standard Sample No. 39d) was melted in a weighed and calibrated quartz flask, *A*, immersed in a bath of liquid petrolatum at 140° C. After a suitable amount of the acid had been introduced and melted in the flask, the latter was taken out of the heating bath, cleaned, and allowed to cool in a desiccator. On solidifying, the mass of benzoic acid developed numerous cracks and separated from the flask. When cool, the flask was stoppered and reweighed to obtain the weight of the sample. A current of air, dried and freed from carbon dioxide by passing through concentrated sulphuric acid, sodium hydroxide on asbestos, and magnesium perchlorate trihydrate, in the order named, was then blown into the neck of the flask for a few minutes. Then the lubricated ground Pyrex capillary stopper *B*, which was sealed to the volume-regulating manometer *C* and the pressure-regulating manometer *E*, was inserted. The apparatus was next placed in a water thermostat having a plate-glass front and back and provided with a heater, cooling coil, stirrer, and a mercury regulator, the latter connected with a vibrator and the electron tube circuit described by Beaver and Beaver.[1] The extreme variations in temperature at a given setting were less than 0.01°. The absolute value of the temperature was measured to 0.1°. The volume of the flask, capillary, and tube to the mark D had been previously determined by calibration. Manometer C contained butyl phthalate and manometer E contained mercury. The tube F was connected to the apparatus by means of rubber tubing at G. The purpose of F was to regulate the pressure so as always to bring the meniscus of the butyl phthalate to the mark D before taking a measurement, and thus have the total volume of the system equal to the calibrated volume. Butyl phthalate was found to be advantageous for this purpose because of its low vapor pressure and density.

From the weight of benzoic acid and its density,[2] the volume of benzoic acid was known. The volume of air at 15° was obtained by subtracting the volume of benzoic acid from the total calibrated volume. From a measurement of the pressure, the PV product for the air at 15° and the number of moles of air present were calculated. On raising the temperature to another fixed value the benzoic acid expanded and the air was compressed. Since the number of moles of air remained constant, a measurement of the pressure at the second temperature permitted the calculation of the corresponding volume of the air by means of the perfect gas law. The volume of the benzoic acid at the second temperature was then obtained by subtracting the air volume from the calibrated volume. The expansion of the quartz flask and Pyrex capillary was negligible for the accuracy desired in this work. The compressibility of benzoic acid over the small pressure range involved in the measurements is obviously negligible and its vapor pressure [3] is considerably less than 0.1 mm at 30°.

TABLE 1.—*The coefficient of expansion of benzoic acid*

[Weight of benzoic acid in vacuo 185.27 g]

Temperature	Pressure	Volume air	Volume solid	γ	Volume solid, calculated from average
° C.	*mm Hg*	*ml*	*ml*		
30	762.5	27.33	147.48	0.000523	---------
25	739.5	27.72	147.09		147.1
20	717.8	28.08	146.73		146.7
15	695.8	28.47	146.34		---------
20	716.9	28.11	146.70	0.000514	146.7
25	739.0	27.74	147.07		147.1
30	761.9	27.35	147.46		---------

Average γ, 0.00052.

The results of one series of measurements are shown in Table 1. After taking measurements at successively lower intervals of 5° between 30° and 15°, the process was reversed by raising the temperature by 5° intervals from 15° to 30° in order to approach the equilibrium from both sides. The coefficient γ was calculated by means of the equation $V_t = V_o\ (1 + \gamma t)$ in which V_t is the volume of any given weight of benzoic acid at the centigrade temperature t, V_0 is its volume at 0° C. and γ is the coefficient of cubical expansion, $\frac{1}{V_0}\left(\frac{\Delta V}{\Delta t}\right)$. The average value of γ between 15° and 30° was found to be 0.00052 per degree C. The linearity of the expansion and the precision of the results can be seen from the last column of the table in which the volume of the benzoic acid as calculated from the average value of γ is given for comparison with the measured volume.

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[1] Beaver and Beaver, J. Ind. Eng. Chem., vol. 15, p. 359; 1923.

[2] 1.266 at 15° C. Int. Crit. Tables, vol. 1, p. 208.

[3] Int. Crit. Tables, vol. 3, p. 208.

The author desires to express appreciation to E. W. Washburn, chief of the chemistry division of this bureau, for suggesting the method of measurement.

WASHINGTON, September 30, 1931.